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Optical Limiting: An Overview
A State of the Art Report

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13. ABSTRACT

This report intends to elucidate to the non expert in the field of optical limiting, the physical phenomena responsible for optical limiting behavior and the measurements routinely made to characterize the performance of nonlinear materials. A simplified configuration of these materials as protective optical systems, is illustrated. The report also provides a sketchy background on work in the field of molecular engineering, that enhances the performance of nonlinear materials and adapts them to real world applications.

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Preface

This State of the Art Review was conducted by the Advanced Materials and Processes Technology Information Analysis Center (AMPTIAC), and presents an overview of Optical Limiting and related topics.

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In the area of optical and special function materials, AMPTIAC serves as the DOD's central source of engineering and technical data and research and development information on non-linear optical films, infrared absorptive materials, radar absorbing materials and structures, sensor window materials and other specialty materials for optics applications. Emphasis is placed on those materials used in critical optical and thermal applications and/or in other stringent environments.

Subject areas covered include optical limiting, theory of nonlinear behavior, recent research history of nonlinear optical thin films, optical characterization of organic optical limiters, and implementation of sensor and eye protective optical limiters. Properties for other materials, such as metals, ceramics, organics and high temperature materials are covered by AMPTIAC in similar fashion.

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1.0   EXECUTIVE SUMMARY

The present report intends to elucidate to the non-expert in the field of optical limiting the physical phenomena responsible for optical limiting behavior, and the measurements routinely made to characterize the performance of nonlinear materials. A simplified configuration of these materials as protective optical systems, is illustrated. The report also provides a brief background on work in the field of molecular engineering, that enhances the performance of nonlinear materials and adapts them to real world applications.

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2.0   OPTICAL LIMITING

Optical properties of materials are independent of the intensity of the illumination at low light intensities. In a case such as this, light waves pass through the medium without interaction. If the illumination is strong (e.g., laser), the optical properties of the medium may become a function of the interaction between the medium and the optical wave. The characterization of this behavior becomes the realm of nonlinear optics (NLO). NLO technology supplies useful information about the structure and properties of chemicals, and is utilized in the production of protective devices against the damaging effects of strong radiation.

The design of NLO materials requires understanding of quantum chemistry. The empirical search for a suitable formula can be simplified by prior calculations of excited state energies, energy relaxation and transfer rates, molecule-environment interactions and excited states chemistry.[33]

The synthesis of materials for non-linear applications is based on knowledge of electronic structures and properties.[33]

The mechanical models of molecules (one spring for each vibrational degree of freedom) do not provide information about the electronic structures, that is necessary for the design of molecules in the field of NLO.

Quantum mechanics theory throws light on the electronic structures of molecules and elucidates the interaction of electromagnetic radiation with matter.

2.1   Interaction of Electromagnetic Radiation with Matter

The electromagnetic radiation is a form of energy that has dual wave-particle properties. Refraction, reflection, reinforcement and diffractive interference are wave properties. The photon is the particle that travels through space at the speed of light. When gaps through which light passes are small in comparison with the wavelength, one invokes the wave properties, but if these gaps are large compared to the wavelength of the passing radiation, that radiation can be treated as a corpuscular concept.[30]

The electromagnetic wave has an electric component and a magnetic component. The two components oscillate in planes perpendicular to each other, and perpendicular to the direction of propagation of radiation. Due to its ability to transfer energy, the electric component is the only active one in interaction with matter.

The positively-charged particles, in this case the ions, have a much larger mass than the electrons. Consequently, for high optical frequencies (in the ultraviolet and visible ranges) it is the electron motion and its interaction with the optical electric field that has significance. The electron's response to the applied field is that of a particle in an anharmonic potential well.

2.2 Atomic Absorption of Electromagnetic Radiation

To explain absorption of electromagnetic radiation by complicated molecules of optical limiting materials, one needs to understand first atomic interaction with radiation. Consequently, it is necessary to elucidate the quantum theory, which has many applications in physics and chemistry.

Plank established that an oscillator is unable to absorb or emit energy continuously, but that the energy is emitted or absorbed as integral multiples of a definite amount depending on the frequency of the oscillator. Accordingly, the energy of the quantum (ε)

is given by the formula $\varepsilon = h\nu$, where h is Plank's constant and ν is the frequency of the oscillator. Plank's constant is also known as the 'action constant' because it has the dimensions of energy * time.

Einstein made the connection between the quantum theory and the radiation that propagated through space, suggesting that radiation is absorbed and emitted in quanta, and that it propagates through space with the velocity of light, in definite quanta or photons with energy $h\nu$, where ν is the frequency of the radiation. Assuming that radiation manifests itself both as wave and as particle, Einstein deduced the equation

$h\nu = (\frac{1}{2}) mv^2 + P$ for the photoelectric effect.[30] $h\nu$, the energy of the photon of the incident radiation, is the sum of the kinetic energy $(\frac{1}{2}) mv^2$ (of the emitted electron, when the electromagnetic radiation interacts with the atom) and the energy P required to release the electron from the metal. The condition for the photoelectric emission of the electron is that $h\nu > P$, in other words, that ν has a minimum threshold value, ν_0, so that

$$h\nu = (\tfrac{1}{2}) mv^2 + h\nu_0 \text{ or } (\tfrac{1}{2}) mv^2 = h (\nu - \nu_0)$$

Atomic spectra are distinct lines occupying definite positions with definite wavelengths. The atomic spectra are obtained by heating a solid to incandescence, thus causing it to emit a continuous set of wavelengths.

The molecular spectra are band spectra, or collections of closely spaced lines.

The information about electrons is obtained from atomic spectra, due to the fact that such spectra indicate the energy required to ionize atoms (extract electrons under the influence of powerful electric discharge).

Spectral series are series of lines produced through the ionization of an atom or an ion.

The importance of these series stems from the observation that when atomic volumes of the elements are plotted against their respective atomic weights, or atomic numbers, the gradient represents waves corresponding to the periods of the periodic table. This suggests that the periodicity of the physical properties of the element is the result of the volume occupied by the atom of that element. The spectra of elements within the same group of the periodic table are similar. In fact, the analysis of the spectrum of one element in the group can be used to analyze the spectra of the other elements in the same group. Physical properties of elements are a function of the way the electrons are arranged within the atom. Since physical properties of elements occur with periodicity, it is correct to assume that groupings of electrons are periodical in nature. Throughout the periodic table of elements, the number of electrons increases by one unit, as the atom

increases in atomic number. This suggests that electrons arrange themselves in stable groups or shells, and the extra electrons are the electrons that do not fit within a completed (stable) group. The extra electrons are called the optical electrons or valence electrons, and they determine the chemical properties of the individual elements.

When atoms absorb energy (e.g., high temperature, or electrical discharge), excitation occurs, and the electron can jump from an inner (lower energy level) orbit, to higher energy levels (outer orbits). Such a jump can be observed and analyzed in a spectrum.

The simplest example is that of hydrogen atom, that has one electron rotating in a circular orbit about the nucleus. The analysis of spectrum led to the observation that many lines consist of groups of two, three or more lines close together. It has been suggested [34], that an electron rotates about its own axis contributing to the angular momentum that explains the spectral lines. This momentum is quantized (because the spectrum is made of definite lines) and can only have two values or multiples of those values: $+(1/2)$ or $-(1/2)$. The plus or minus indicate that the electron can spin clock wise or anti-clock wise.

2.3   Wave Mechanics and Spectral Lines

When one speaks of electrons, one discusses the probability of the position of the electron within the atom. Consequently, the concept of orbit and the emission of energy due to the electron's jump from one orbit to another cannot be applied. The quantum transition between two orbits then, can be thought of as the difference in frequency between two states of the same atom. Two models of the atoms, Heisenberg matrix mechanics (purely mathematical, without an atom model), and Schrödinger wave mechanics, are utilized to explain the atomic structure. Schrödinger's model assumes that each particle is associated with a wave, and that the wave length $\lambda = h/mv$, where mv is the momentum of the particle, and h is Plank constant.

Since it is assumed that the electron moves in a circular orbit round the nucleus, for the wave motion of the electron to stay in phase, the circumference of the circle must be an integral (n) number of wave lengths: $2\pi r = n\lambda = nh/mv$;

and the angular momentum is an integral (n) number of $h/2\pi$: $mvr = n(h/2\pi)$

The Schrödinger equation system provides solutions to both the nuclear and the electronic movement. Solutions to the nuclear equation explain sets of vibrational wavefunctions and are important in determining optical properties such as lineshapes.[33] However, for determining designs of NLO molecules, they are not taken into account in the present report.

For better understanding, the Schrödinger equation should be initially examined by considering the simplest wave motion, namely the vibrations of a stretched string. If one assumes motion in three directions, represented by the Cartesian coordinates x, y, and z, and $\psi(x, y, z)$ is the amplitude function corresponding to the three coordinates in the Cartesian system, the equation becomes

Equation 1 $$\partial^2\psi/\partial x^2) + (\partial^2\psi/\partial y^2) + (\partial^2\psi/\partial z^2) = -(4\pi^2/\lambda^2)\,\psi$$

where ψ is short for $\psi(x, y, z)$, the amplitude function for the three coordinates. ∇^2 is the differential (Laplacian) operator, i.e., $\nabla^2 = (\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)$. By substituting the expression for Laplacian in Equation 1:

Equation 2 $$\nabla^2\psi = -(4\pi^2/\lambda^2)\,\psi$$

Since $\lambda = h/mv$, the equation becomes

Equation 3 $$\nabla^2\psi = -(4\pi^2 m^2 v^2/h^2)\,\psi$$

where m is the mass and v is the velocity of the particle (different from the velocity of propagation u of the hypothetical wave motion).

If E is the total energy of the particle, and U is the potential energy, the kinetic energy $(mv^2/2)$ of the moving particle is given by: $E - U = mv^2/2$. Combining this with the previous equation, the Schrödinger equation is obtained:

Equation 4 $$\nabla^2\psi + (8\pi^2 m/h^2)(E - U)\,\psi = 0$$

The Schrödinger equation is used to calculate values related to the atomic and the molecular structure. Since orbits represent specific positions (an incongruous concept in quantum mechanics), one should regard ψ^2 as the electrical charge density, a constant value in a stationary state (in which the atom does not radiate). When there is electromagnetic radiation of matter (and absorption of energy), the function ψ changes periodically, and the frequency of this change depends on the strength of the applied electromagnetic field. If ψ^2 is the charge density, the variation in its distribution is accompanied by energy emission.

2.4 The Physical Significance of the Wave Function

In the case of sound or light wave propagation, the square of the amplitude is proportional to the intensity of the sound or of the light, respectively.[30]

Through analogy, the probability of finding the electron at a particular point in space is proportional to the square of the wave function, i.e., to ψ^2. Schrödinger suggested that the value of ψ^2 at a specific point is the electrical charge density at that point (a cloud of electricity varying with the location). M. Born's theory of statistical interpretation has been ultimately adopted. Accordingly, the electron is still considered a particle, and ψ^2 at a particular point is the statistical probability of finding the electron in that particular point.

The probability, P, of finding the electron at the point (x, y, z) is given by

Equation 5 $$P = \psi(x, y, z)\,\psi^*(x, y, z)$$

Where ψ^* is the complex conjugate of ψ. Since the probability of finding an electron at any point cannot be an imaginary value, ψ must be multiplied by its complex conjugate. If $\psi = \psi^*$, the probability of finding the electron in any place, becomes ψ^2.

The duality in the interpretation of ψ allows one to regard the electron as a particle, while using the wave equation to calculate the probability of finding the electron at any given point.

2.5   The Electronic Structure of Atoms [31]

The foundation of electronic structure in an atom is derived from the simplest atom, the hydrogen atom. The wave equation for hydrogen, written in terms of spherical polar coordinates r, θ and Φ (which are related to the Cartesian coordinates x, y, z) is of the form

Equation 6 $(1/r^2)(\partial/\partial r)(r^2 \partial \psi/\partial r) + (1/ r^2 \sin \theta)(\partial/\partial \theta)(\sin \theta \, \partial \psi/\partial \theta) +$

$$+ (1/ r^2 \sin^2 \theta)(\partial^2 \psi/\partial \Phi^2) + (8\pi^2 \mu/h^2)(E + e^2/r) \, \Psi = 0$$

Solution to this equation is of the form $\Psi = R(r)\Theta(\theta) \, \Phi (\varphi)$

Ψ is a function of all three spherical coordinates r, θ and φ. By substituting the expression of Ψ in the equation above, it is possible to obtain an equation in which LHS (left hand side) depends only on r, while RHS (right hand side) is a function of θ and φ.

Equation 7 $(1/R) \, \partial/\partial r \, (r^2 \partial R/\partial r) + (8\pi^2 \mu/h^2)(E + e^2/r) \, r^2 =$

$$= (-1/\Theta \sin \theta) \, (d/d\theta) \, (\sin \theta \, d\Theta/d\theta) - (1/\Phi \sin^2 \theta) \, (d^2 \Phi/d\varphi^2)$$

For the above equation to be true for all values of r, θ, and φ, each side of the equation must be equal to a constant, λ. By separating the two sides of the equation, and equating them to λ, two more equations are obtained

Equation 8 $(\sin\theta/\Theta) \, (d/d\theta) \, (\sin\theta d\Theta/d\theta) + \lambda \sin^2\theta = (-1/\Phi) \, (d^2\Phi/d\varphi^2)$

and

Equation 9 $(1/r^2)(d/dr)(r^2 dR'/dr) + [(8\pi^2 m/ h^2)(E + e^2/r)) - \lambda / r^2] \, R = 0$

Further separation of one of the above equations, by imposing the condition that both sides will be equal to a constant, m, gives two more equations

Equation 10 $(\sin\theta/\Theta) \, (d/d\theta) \, (\sin\theta d\Theta/d\theta) + \lambda \sin^2\theta = m^2$

Equation 11 $d^2\Phi/d\varphi^2 = - m^2\Phi$, where is a constant.

It is possible to solve the last equation, whereby $\Phi= (2\circ)^{-1/2} \exp (im\varphi)$, in which m is a positive or negative integer, therefore it must be a quantum number.

Solutions for Θ are functions of the quantum numbers l and m. l can only have positive integral values while m can be both positive and negative:

$l = 0, 1, 2, 3,....$

$m = 1, (l-1), (l-2), (l-3),......,0, -1,.....,-1$

By substituting λ with $l(l+1)$ in Equation 9, it is possible to calculate the quantized energy levels

Equation 12 $$E_n = (-1/n^2)\ (2\pi^2\mu^2 e^4/h^2)$$

where μ is a constant and n is another quantum number that can take values from 1 to ∞.
$l = (n-1), (n-2), ..., 0$

The energy levels of hydrogen depend on the quantum number n only (because the electron revolves round the nucleus in a circular orbit, of a constant radius), therefore n is the principal quantum number.

The solutions to the Schrödinger equation are wave functions called orbitals, and they describe the spacial distribution of electron density about the nucleus. Each function is uniquely identified by the quantum numbers n, l and m.

The three quantum numbers n, l and m obtained from the Schrödinger equation have a physical meaning. The n value gives a measure of the energy of an electron in an orbital. When n = 1, the energy level is the most negative (lowest). When n = ∞, the energy becomes zero, and the electron is not bound any longer to the nucleus. The n value is also a measure of the mean radial distance of the electron density from the nucleus.

The quantum number l is a measure of the angular momentum of the electron, although it is impossible to visualize this, since the electron is not a discrete body with a specific position and velocity.

The quantum number m, expresses the position of the angular momentum of the orbital relative to a fixed direction. m= 1, (1 – 1), (1 – 2),.....-(1 – 1), -1

2.6   The s, p, d Orbitals [31,32,33]

The shape of each orbital is determined by both the radial and the angular components of the wave function.

The s orbital is a function of the radius only, and it exists in every principal shell (K, L, M,...). The s orbitals are spherically symmetric , with an angular wave function independent of θ and Φ.

The p orbitals exist in an atom with n => 2. The p orbitals are not independent of θ and Φ, therefore they are not spherically symmetric. The p orbitals have three components, of equal energies (2p) classified as p_x, p_y and p_z. The present report focuses on s and p orbitals.

```
4p  ———

                                        4d  — — — — —

4s  —

        3p———

3s  —

        2p———

2s  —

1s  —
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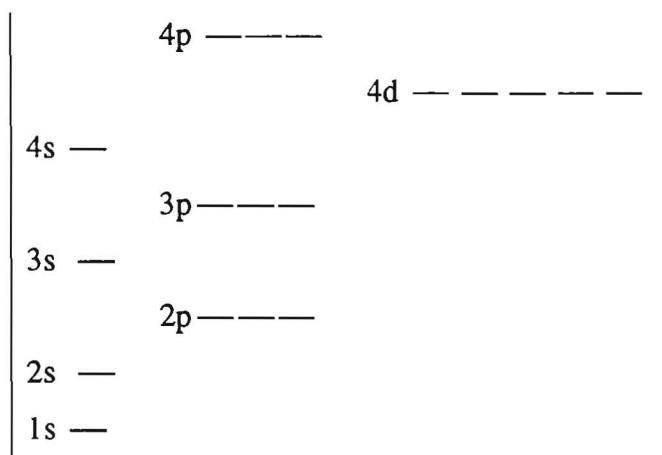
Figure 1   Diagram of the Energy Levels of the Hydrogen-Like Atomic Orbitals[31]

The 1s and 2s orbitals are spherically symmetrical, while the three p orbitals (p_x, p_y, p_z) are not.

The 3s and 3p are similar to 2s and 2p, but have a higher level of energy. The 3d and 4f are not discussed in the present report.

Each electron is graphically represented by the symbol $\uparrow$ and $\downarrow$. Pauli's exclusion principle states that no more than two electrons can occupy a particular orbital, and the condition for the two electrons to be in the same orbital is that they have opposite spins ($\uparrow\downarrow$).

The ground state configuration of carbon is $(1s)^2 (2s)^2 (2p)^2$

Two paired electrons are on 1s, two, on 2s. The electrons populate 2p in compliance with Hund's rule. Accordingly, if there are two orbitals of the same energy (degenerate orbitals) the two electrons will go into these two separate orbitals, rather than pair up in one orbital.

2.7   The Molecular Orbital (MO) Theory of Bonding

In the case of simple molecules, such as the hydrogen molecule, MO's are formed by overlap of an s orbital from each of the participating atoms. This type of MO is called a σ type and the property that qualifies MO's to belong to a σ category is the cylindrical symmetry about the internuclear axis. Each of the two s orbitals participating in the formation of the molecular bond is symmetrical about the internuclear axis. When two atomic orbitals (s) overlap, they combine to give one low-energy bonding orbital (σ), and one high-energy anti-bonding orbital ($\sigma *$). Two hydrogen atoms fill a σ orbital by participating each with one electron. Any additional electrons go on the high-energy $\sigma *$ orbital, causing not bonding, but repulsion between the atoms.

The best theoretical criterion for the formation of an electron pair bond is the release of energy when the bond is formed. Quantitative calculations of energy release during bond formations are tedious. However, from a qualitative point of view, it is possible to

explain why a good overlap between the orbitals of participating electrons makes strong bonding. The more the two orbitals overlap, the more the bonding electrons concentrate between the nuclei where they can minimize repulsion and maximize attraction between themselves and the nuclei.

2.8   Carbon Atom and Hybridization

The carbon atom has the divalent ground state configuration s^2p^2. It is necessary to promote carbon to the tetravalent state sp^3, to form its compounds (e.g., CH_4). The sp^3 configuration is actually $2s2p_x2p_y2p_z$.

In the case of CH_4, it is expected that three hydrogen atoms will form bonds with the p_x,

p_y, p_z orbital, thus having their 1s orbitals lye along the carbon x, y and z axes. The fourth hydrogen atom is expected to bond to carbon's s orbital, and become equidistantly situated from the other three hydrogen atoms.

This set of four equivalently directed orbitals is an example of a set of hybrid orbitals, specifically, sp^3 hybrids. The hybridization involves determining which combinations of the s and p orbitals are more effective than the individual s and p orbitals. In general, it is said about carbon that it has sp^3 hybridization. The process of hybridization in the case of carbon has two stages: (1) the s orbital and the three p orbitals are hybridized to produce four sp^3 hybrids, each occupied by one electron, and (2) preferred orientations of the electrons in atoms are destroyed, so that they can be paired with electron spins of other atoms. Both stages of hybridization are endothermic.

Carbon bonds in saturated compounds (alkanes and their derivatives with normal tetrahedral angles) are of the sp^3 σ type. Carbon-carbon double bonds in unsaturated compounds (such as the one in ethylene), have different type of hybridization.

An s orbital is of $\_$ character and it is not so denoted. However, a p orbital has x, y and z directions. If the internuclear axis is defined as the z axis, the s-p_z hybrid orbitals combine to give $\_$ MO's, and the p_z orbital lying along the molecular axis is called a $p\_$ orbital. In a case such as this, the p_x and p_y axes are not lying along the MO axis. They become $p\pi$ orbitals. The π overlap is sidewise overlap of orbitals (as opposed to $\_$ endwise overlap).
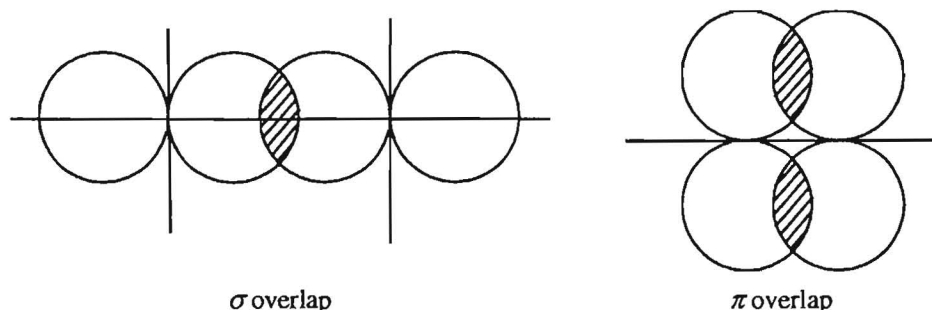

σ overlap π overlap

Figure 2   Schematic Representation of σ and π Overlap of p Orbitals[31]

Two pπ orbitals combine into a bonding π MO expressed as pπ (1) + p∘(2), denoted as ∘ and an antibonding π MO, pπ (1) - pπ (2), denoted as π*.

2.9   The Benzene Model

Benzene has, according to X-ray diffraction and spectroscopic measurements, a flat molecular structure with six carbon atoms, 1.397 Å apart, in a hexagonal ring.[3] Six hydrogen atoms are bound to carbon atoms in 1.09 Å long bonds.

Each carbon atom in the benzene molecule uses its s, p_x and p_y orbitals and three of its electrons to form the σ bonds. Each carbon atom has an additional p_z orbital (which is a pπ- type orbital). There are six carbon atoms in the benzene ring, with six π electrons being associated with all six carbons in a region above and below the plane of the ring. Consequently, the six electrons are delocalized among the six centers, thus creating a more stable, continuous π bonding with all six carbon atoms rather than a localized one between adjacent carbon atoms. Figure 3 represents the benzene molecule as a hybrid of the valence-bond structures [1], [2], [3], [4], and [5]. These five structures are called resonance structures, and do not have independent existence. In reality, the energy of the benzene molecule is lower than any of the five contributing structures. The double-headed arrows between two consecutive models indicate different electron-pairing schemes rather than substances in equilibrium. The first two structures [1] and [2], contribute much more to over-all bonding than the [3], [4], and [5]. The theory of resonance structure assumes that all the structures contributing to one hybrid have identical spatial arrangement. Consequently, [3], [4], and [5] cannot be considered bicyclohexadiene despite their similar electron pairing scheme. The bicyclohexadiene is a nonplanar molecule with different bond lengths and bond angles. The stability gained in benzene by delocalizing the electrons is called the resonance energy (R.E.). The stability of structures like that of benzene, sets these compounds apart from the open-chain conjugated polyenes, in a group called 'aromatic.'

Aromatic compounds exhibit critical properties for nonlinear optical applications. Due to their ∘ bonds, aromatic molecules have large nonresonant susceptibilities, fast response times, low dielectric constants, and large optical nonlinearities.[10]

Electron-Pairing Schemes[32]

The five resonance structures may be
abbreviated by this single representation
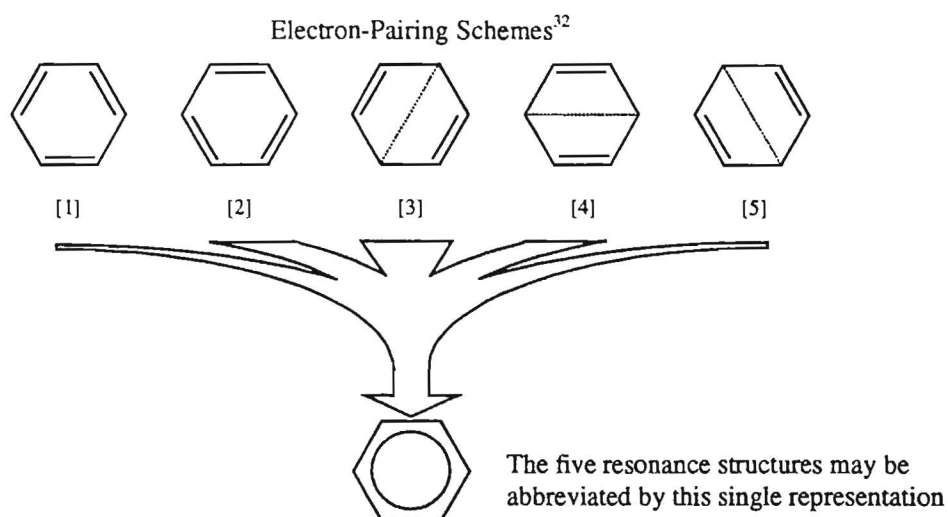
Figure 3 Representations of the Benzene Molecule

Due to their low dielectric constants (because of efficient charge reorganization among the π-electrons), aromatic compounds can be used in electro-optic devices where low frequency ac fields are applied to modulate the refractive index.

2.10   Aromatic Compounds as Optical Limiting Devices

Passive protection has been employed so far, to shelter detection systems and human eye, from high-power laser-induced damage (LID). The term 'passive' means that the optical energy of the laser is used directly by the material, through absorption, refraction, deflection, or scattering of the beam at high input energy.[13] One can produce materials that become opaque at high levels of energy, thus affording protection. However, so far, optical limiting has not been achieved without optical gain (i.e., the entrapment of light in the material).
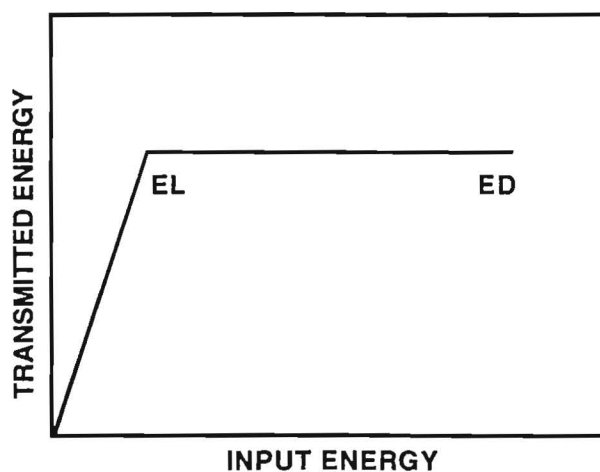
Figure 4 Input-Output Response of an Ideal Optical Limiter

The strongest nonlinear response is achieved by placing the NLO device at focus, but in this position the protective material is likely to suffer laser-induced damage, and a small dynamic range (DR). The Dynamic Range (DR) is defined by the ratio of the input energy at the lowest transmittance (damage threshold), to the input energy corresponding to the linear transmittance. Thus, in terms of Figure 5, DR = ED/EL. The material exhibits linear response at low energy input levels.

The absorption coefficient of certain materials may depend on the intensity of light. Some materials become more transparent with increasing intensity and are known as saturable absorbers, whilst other materials tend to become opaque with increased intensity, and such a property is referred to as Reverse Saturable Absorption (RSA).

Based on their unique chemical structures of o bonding, aromatic molecules exhibit the largest nonresonant optical nonlinearities.[10] This is attributed to efficient charge interchange between the electronic states in the o electron-system of the benzene-type ring.

5 – Level Model
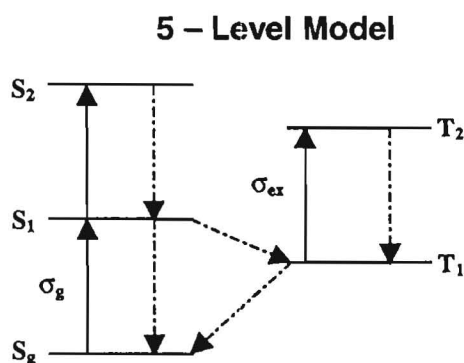
Figure 5 Five Level Diagram of Optical Limiter Photophysics

When a laser of pulse width τ excites the ground state (S_g) of the RSA, to the first singlet state (S_1), intersystem crossings occur to the triplet state (T_1). The conditions for an RSA material to be an efficient nonlinear absorber, are: 1) a high ratio of excited state ($T_1 \rightarrow T_2$) to ground state ($S_g \rightarrow S_1$) absorption cross section ($\sigma_{ex}/\sigma_g \gg 1$), 2) rapid intersystem crossing rate ($\tau_{ISC} \ll \tau$), 3) long conversion lifetime ($\tau_{IC} \ll \tau$), 4) a high intersystem crossing quantum yield ($\varphi_{S1 \rightarrow T1} \sim 1$) and 5) a long triplet lifetime ($\tau_{T1} \gg \tau$). If these conditions are not met, there is no sufficient triplet state population and the result is poor nonlinear absorption.

In the case of the benzene ring in the example below, the conjugated unit is the benzene ring. The benzene ring separates an electron-donor group (D) such as NH_2 from an electron acceptor group (A) such as NO_2. The lowest lying excited state in such a structure involves transfer of charge from NH_2 to NO_2, and a large change in dipole moment.

Figure 6 A Conjugated Benzene Ring

The introduction of an A side chain to the benzene ring increases the flow of π-electrons, augmenting the optical nonlinearity of the material

The origin of the third-order nonlinearity for many organic molecules is the π-conjugated transition. A π-bond exists in organic molecules where two carbon atoms are double-bonded in a planar molecule, as explained in the previous section.

Most of the articles dealing with nonlinear organic molecules discuss what is known as π-conjugation or the π-π* transition.

3.0 THE ORIGIN OF OPTICAL NONLINEARITY[32]

When the illumination is strong, the light waves interact with each other and with the medium they pass through. The laser is used as a cohesive source of illumination, to observe these phenomena. If the medium is regarded as a collection of charged particles, the irradiation causes movements of these particles – positive charges in one direction and negative particles in the other direction – thus inducing polarization (for as long as the medium is considered dielectric).

The previous chapter dealt with atomic and molecular structures, and included information on benzene molecules, with relevance to the topic of this report. This chapter establishes the link between such structures and the nonlinear optics manifested by certain materials.

Equation 13 represents the response of the electron e (similar to that of an oscillator) to the electric field E(t).

When the displacement, x, is large, the restoring force acting on the particle is nonlinear in x. (Mechanically, it is said that the spring becomes distorted and cannot return to its original condition, elastically.)

Equation 13
$$m\frac{d^2x}{dt^2} + \eta\frac{dx}{dt} + m\omega_0^2 x - \text{HOTs} = -eE(t)$$

where the right-hand side of Equation 13 represents the force exerted on the electron, E(t) is the external electromagnetic field, -e is the charge of the electron, θ is a damping constant, and the term $m\varphi_0$ is the spring constant, with φ_0 being the resonant vibrational frequency of the electron, x is the displacement from the mean position, and m, the mass of the electron.

HOTs stands for Higher Order Terms (anharmonic terms) and it is ignored at this point. The harmonic response to an applied electric field is given by the equation

E(t) = $E_0\cos(\varphi t)$ =(1/2) $E_0[\exp(-i\varphi t) + \exp(i\varphi t)]$ where φ is the optical frequency. Substituting this expression into Equation 14.

one obtains a linear equation whose solution is

Equation 14
$$x(t) = \frac{-eE_0}{2m}\frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 + i\omega\Gamma}$$

The dipole moment of the charge pair is then equal to -ex(t). The polarizability of the medium itself in any medium, is the sum of the contributions of all of the individual dipole moments per unit volume, or -Nex(t), where N is the number of oscillators per unit volume. Substituting Equation 14 for x(t) yields

Equation 15
$$P(t) = \frac{Ne^2 E(t)}{m} \frac{1}{\omega_0^2 - \omega^2 + i\omega\Gamma}$$

Equation 15 is usually rewritten as $P(t) = \varepsilon_0 \chi E(t)$, where the complex number χ is the electric susceptibility of the material and ε_0 is the permittivity of free space. The index of refraction and absorption constant of the material are related to the susceptibility in the following manner

Equation 16
$$n^2 = 1 + \text{Re}(\chi)$$

Equation 17
$$\kappa = \frac{\omega}{c} \text{Im}(\chi)$$

When the magnitude of the incident electromagnetic field is large, the contributions due to the higher-order terms must be taken into account. At this point there is no longer a closed solution to the equation of motion given in Equation 14 or for the polarizability, given in Equation 15. However, the polarizability may be expanded as a power series in E as

Equation 18
$$P_i = \varepsilon_0 \left(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \text{HOTs} \right)$$

where the susceptibility has been written in its tensor form, and the superscript in parentheses represents the order of the susceptibility and the subscript i denotes the axis.

When the anharmonic factors are considered, it is important to determine the magnitude of the incident optical field, in order to measure the nonlinear behavior of atoms and molecules. If the internal field E_a, that bonds electrons and ions is in the range of $3*10^{10}$ V m^{-1}, the intensity of the incident field must be $\sim 10^{14}$ W cm^{-2}. However, if the dipoles oscillate coherently (i.e., in phase with each other), their phases add up to produce an emitted field (the response) of high intensity. In NLO, this constructive interference is called 'phase matching.'

(1) $\chi_{ij}^{(1)}$ connotes the linear susceptibility tensor of the material and represents the low-intensity electromagnetic interactions with the material.

(2) $\chi_{ijk}^{(2)}$ connotes the second-order susceptibility tensor and represents the nonlinear effects due to mixing phenomena, involving the sum and difference frequencies. Examples of these types of phenomena are optical rectification, the Pockels effect, second-harmonic generation, and parametric amplification. Pockels effect is the linear dependence of the susceptibility $\chi_{ijk}^{(2)}$ on the electric field, E, and explains the electro-optic effect.

(3) $\chi_{ijkl}^{(3)}$ is the third-order susceptibility tensor and represents the nonlinear effects due to phenomena such as the Kerr effect, d.c.-induced second-harmonic generation, third-harmonic generation, coherent anti-Stokes Raman scattering, self-focusing, degenerate four-wave mixing, and self-induced birefringence. Kerr

effect provides a mechanism for light controlled by a beam. An intense electromagnetic field can change the refractive index of the material it passes through, thus influencing its own propagation, or the propagation of another beam. An interesting occurrence is that for materials with inversion symmetry, all the even-ordered susceptibilities disappear. The simplest inversion symmetry, the inversion of the molecule, can be determined by drawing a line through the center of the molecule. If one half of the molecule is the mirror image of the other half, irrespectively of how the line is drawn, the molecule has inversion symmetry. An example of a compound with inversion symmetry is benzene. If a line is drawn from any vertex through the center of the molecule to the opposing vertex or from any side through the center to the opposing side, the two halves will be mirror images of each other.

Since the incident electromagnetic fields can have the same or different frequencies (including a zero-frequency, or d.c. term, the nonlinear susceptibility is often written as a function of those frequencies, for example $\chi(\varphi_s; \varphi_1, \varphi_2)$, where $\varphi_s = \varphi_1 + \varphi_2$. Equation 18 can then be separated and written as

Equation 19
$$P(\omega)_i^{(1)} = \epsilon_0 \chi_{ij}(\omega_1) E_j(\omega_1)$$

Equation 20
$$P(\omega)_i^{(2)} = \epsilon_0 \chi_{ijk}(\omega_s; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$$

Plus higher-order terms.

Equation 21
$$P(\omega)_i^{(3)} = \epsilon_0 \chi_{ijkl}(\omega_s; \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3)$$

There is degeneracy associated with χ due to the intrinsic permutation symmetry. For example, the second-order susceptibility can be written as χ_{ijk}, χ_{jki}, or χ_{kji}. Each of these forms represents electromagnetic fields being applied along different axes of the material, and so are distinguishable. However, when not in resonance, the order of the electric fields is not important and the susceptibility does not depend upon the order of the frequencies. Thus, far from resonance, the nonlinear terms are multiplied by a degeneracy factor, g, which varies on the order of the nonlinearity and the frequencies of the incident E-fields. The second- third- and successive higher-order terms are rewritten as

Equation 22
$$P(\omega)_i^{(2)} = \epsilon_0\, g\chi_{ijk}(\omega_s; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$$

Equation 23
$$P(\omega)_i^{(3)} = \epsilon_0\, g\chi_{ijkl}(\omega_s; \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3)$$

where $g = 2^{l+m-n}p$. Here, p is the number of distinct permutations, n is the order of the nonlinearity, m is the number of incident fields that are dc, and l is a number set to 1 if $\varphi_s \neq 0$ or 0 if it is. The following are examples in the calculation of g.

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First, consider the second-order sum- and difference-frequency mixing, for which the susceptibility is denoted as $\chi(\varphi_3; \varphi_1, \pm \varphi_2)$ and the subscripts left off for neatness. Since this is second-order and since there are 2 distinct frequencies, p = 2. Neither of the E-fields are dc, so m = 0, and since the sum or difference of the two frequencies do not equal zero, l = 1. The degeneracy factor for this is g = 1.

Next, consider the third-order effect third-harmonic generation, for which the susceptibility is denoted as $\chi(3\varphi; \varphi, \varphi, \varphi)$. Here, three fields of the same frequency are mixed. Since interchanging the axes at which the E-fields impinge, does not alter the order, p = 1. There are no incident fields that are dc, so m = 0, and l = 1 since the resultant frequency is non-zero. The degeneracy factor is then $(1)(2^{1+0-3})$, or 1/4. Table 1 lists a number of nonlinear phenomena with their degeneracies.

Table 1 NLO Processes and Susceptibilities

Susceptibility	Order	Degeneracy	Process
$\chi_{ijk}(2\varphi; \varphi, \varphi)$	2	½	2nd Harmonic Generation (SHG)
$\chi_{ijk}(0; \varphi, -\varphi)$	2	½	Optical Rectification
$\chi_{ijk}(-\varphi; 0, \varphi)$	2	2	Linear Pockel's Effect
$\chi_{ijk}(-\varphi_p \pm \varphi_s; \varphi_p, \varphi_s)$	2	1	Parametric Sum/Difference
$\chi_{ijkl}(-3\varphi; \varphi, \varphi, \varphi)$	3	1/4	3rd Harmonic Generation
$\chi_{ijkl}(-2\varphi; 0, \varphi, \varphi)$	3	3/4	Field-Induced SHG
$\chi_{ijkl}(-\varphi; 0, 0, \varphi)$	3	3	d.c. Kerr Effect
$\chi_{ijkl}(-\varphi_3; \pm \varphi_1, \varphi_2, \varphi_2)$	3	3/4	3rd-Order Sum/Difference Mixing
$\chi_{ijkl}(-\varphi; \varphi, \varphi, -\varphi)$	3	3/4	Self-Focusing
$\chi_{ijkl}(-\varphi_1; -\varphi_2, \varphi_2, \varphi_1)$	3	3/2	Two-Photon Absorption
$\chi_{ijkl}(\varphi_{AS}; \varphi_P, \varphi_P, \varphi_S)$	3	3/4	Coherent Anti-Stokes Raman

4.0   RECENT HISTORY OF NLO ORGANIC THIN FILM RESEARCH

The presence of a third-order NLO effect has been examined in many types of organic materials.   Linear delocalized π-conjugated polymers such as polyacetylene and polydiacetylene that were known to also have electric conducting properties were also observed to possess high linear optical susceptibilities along the direction of their chains. However, these polymers are difficult to process since they are normally crystalline and are insoluble in most organic solvents.

Similar investigations were made with soluble conjugated polymers, such as poly(arylene vinylene) and variations of its chemical structure such as poly(phenylenevinylene), PPV, and poly(2,5-thienylenevinylene), PTV.   These compounds yielded third-order susceptibilities on the order of 7.8×10^{-12} and 3.2×10^{-11} esu, respectively, which was high for processable polymeric material. The term esu stands for electrostatic units. In this system, the susceptibility, χ^n is given in units of $(cm \ statvolt^{-1})^{n-1}$. The conversion into SI units is $\chi^n (SI) = 4 \pi \chi^n (esu)/(10^{-4}c)^{n-1}$. Following the work on PPV and PTV, the derivative poly(2,5,-dimethoxyparaphenyl- vinylene), MOPPV, was developed. This polymer consisted of a phenyl ring with two methoxy groups that increased the electron density along the chain of the polymer which was thought to enhance its third-order susceptibility. This was verified when the polymer was evaluated to have a χ^3 of 5.4×10^{-11} esu.

This work was followed by investigations into the nonlinear characteristics of other polymers such as polyimide, polybenzoxazole, and polybenzobisthiazole.   Still, other investigations were made into poly(2,5-thiophene)[1] and its derivatives[2].   One such derivative, referred to as PMTBQ, was reported as having a third-order susceptibility of 4.6×10^{-9} esu[3].   Reference 1 presents an excellent paper on the history of nonlinear optical organic materials.

The key to the third-order nonlinear behavior of some polymers is the conjugated bond in the monomer (the smallest indivisible link in a polymeric chain) species. Investigation has shown that monomers with higher and higher ratios of these bonds produced larger and larger susceptibilities and this in turn has led to the investigation of macrocyclic molecules such as phthalocyanines and porphyrins.

The chemical structure of porphyrin is shown in Figure 7.   This molecule has 9 conjugated π-bonds in its structure. In Figure 7, these are represented by the sets of parallel lines (double bonds) that connect some of the outer vertices of the structure. By attaching other molecules to the macrocyclic ring structure, researchers have been able to improve not only its optical performance but its heating stability and damage threshold as well. Examples of these are given in Figure 8.

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[1] Prasad, P.N., Swiatkiewicz, J., and Pfleger, J., *Mol. Cryst. Liq. Cryst.*, 160, 53 (1988).
[2] Jenekhe, S.A. and Flom, S.R., *Appl. Phys. Lett.* 54 (25), 19 June (1989).
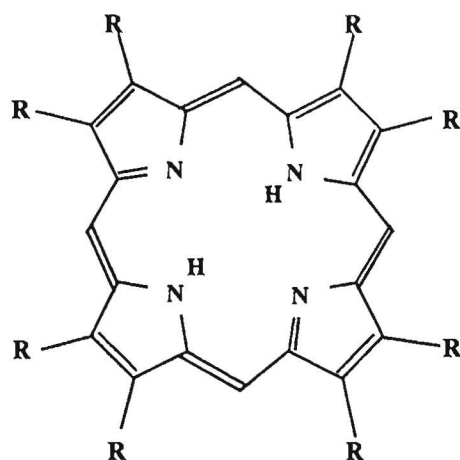
Figure 7 Chemical Structure of Porphyrin.

(A)

(B)
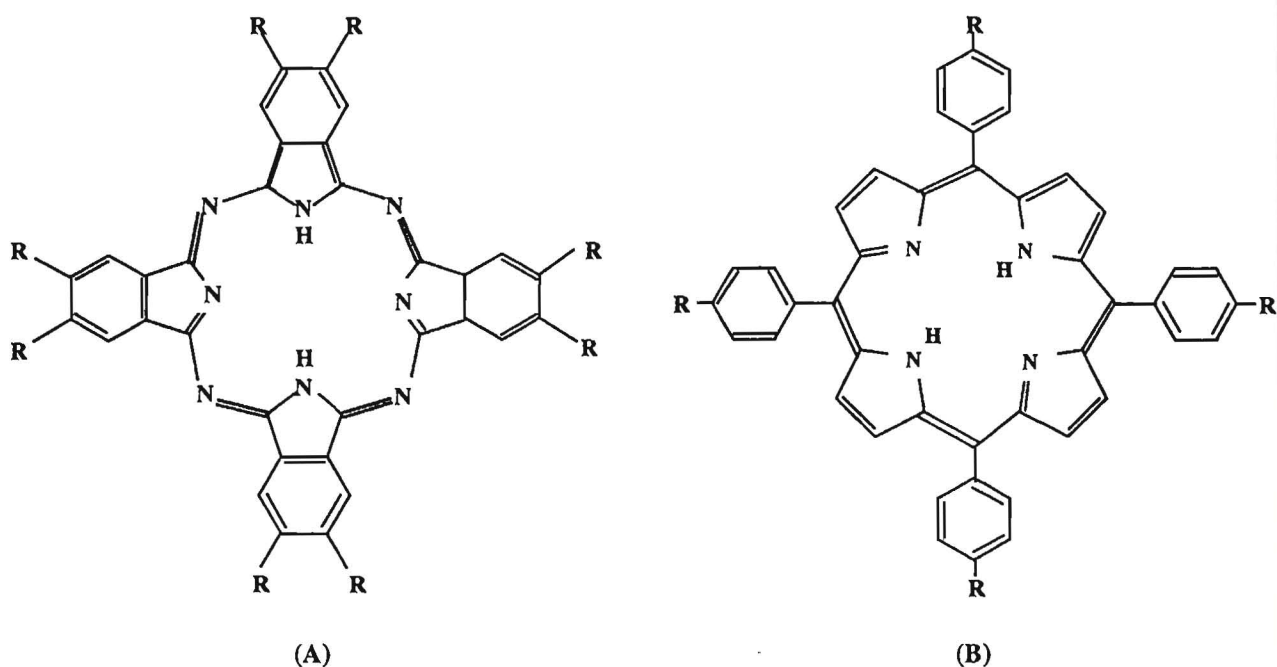
Figure 8 Chemical Structure of Tetrabenzoporphyrin (A) and Tetraphenylporphyrin (B).

The chemical structure of phthalocyanine is presented in Figure 9, also showing the macrocyclic structure of the molecule and a number of conjugated π-bonds.   As with porphyrin and its derivatives, substituting various donor and acceptor groups will augment the value of the third-order optical susceptibility.   There are two additional modifications to the molecules that are being made that impact their nonlinear properties. First, metals are substituted into the macrocyclic ring structure.   In an investigation of octatetraene (a prototype, delocalized π-system), calculations made implied that virtual transitions between states produced large-chain separation, making predetermined

contributions to molecular third-order susceptibility. This led to the possibility that by introducing large transfer states into a conjugated molecule, the number of states with large charge separations are increased, enhancing the nonlinear susceptibility. By substituting metals into the phthalocyanine compounds, metal-to-ligand and ligand-to-metal charge transfer states are introduced into the molecule[3]. Figure 10 shows what the structure looks like with the introduction of the metal[4].
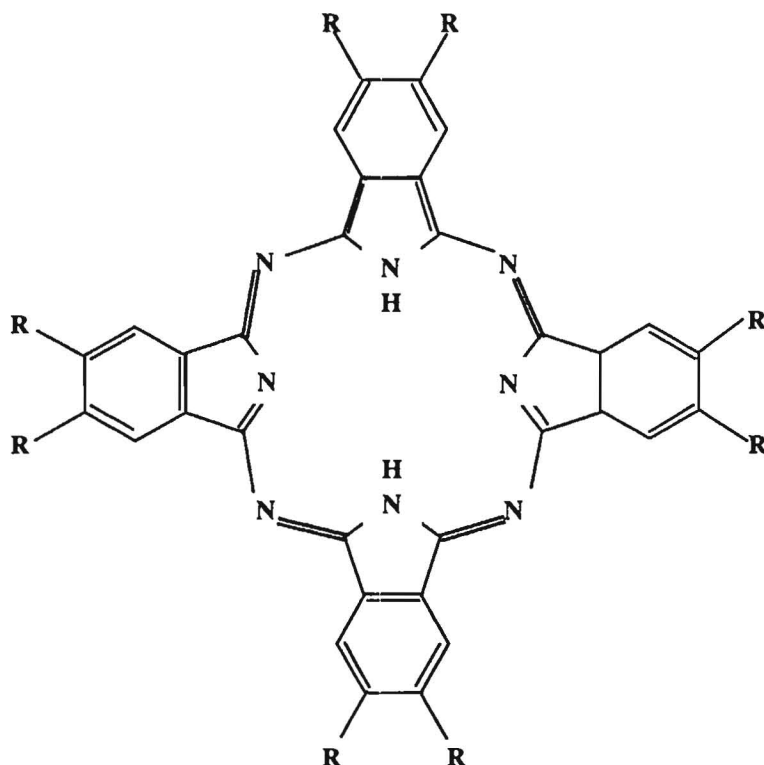

Figure 9 Chemical Structure of Phthalocyanine.

[3] Shirk, J.S., Lindle, J.R., Bartoli, F.J., Hoffman, C.A., Kafafi, Z.H., and Snow, A.W., *Appl. Phys. Lett.* 55 (13) 25 Sept. (1989).
[4] Snow, A.W., and Boyle, M.E., **Glassy Organic Dye-Based Optical Materials and Their Method of Preparation**, Dept. of the Navy Report No. ADD017492, 5 Oct. (1994).
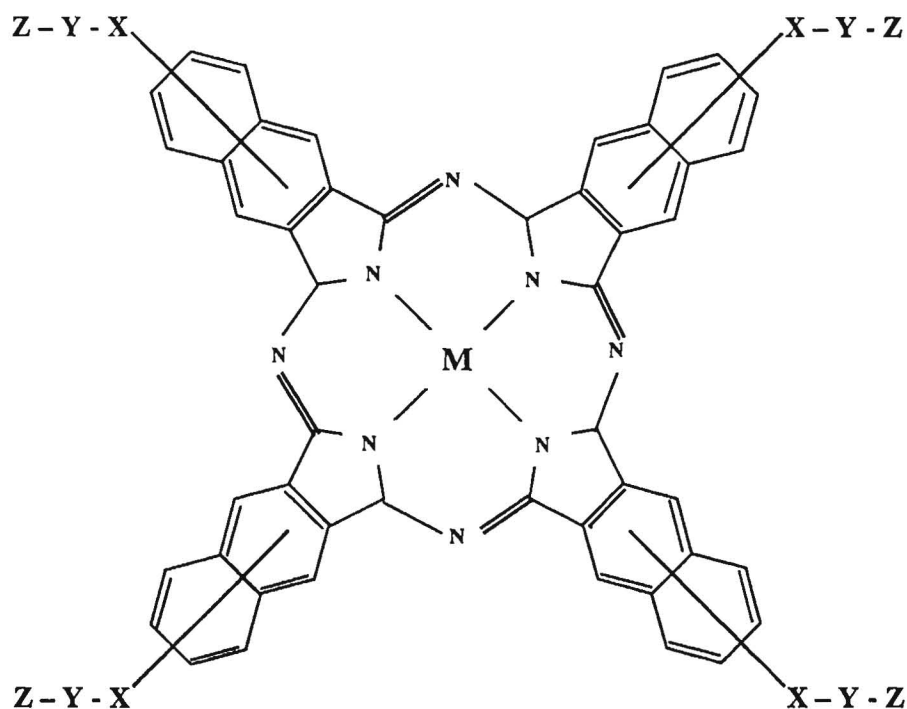
Figure 10 Chemical Structure of Metal-Substituted Phthalocyanine[5]

In Figure 10,

M = Be, Mg, Al, Si, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ge, Rh, Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Pb, Bi, or VO;

X = oxygen or sulfur;

Y = benzene, dibenzene, siloxyl, alkoxy, or alkyl chain (C_1 to C_{16}) including linear, branched, saturated, unsaturated, substituted, unsubstituted, cyclic;

Z = H, OH, OCN, SH, NH_2, NHR, NR_2, carboxylic acid, ester, anhydride, OR', SR', NHR', NR'_2, OCOOCOOR', where R is an alkyl or aryl and R' is a monomeric repeating unit;

In addition to planar phthalocyanine compounds, recent work has been devoted to investigating the nonlinear optical properties of sandwich-like compounds with a substituted metal centered between two phthalocyanine rings. These compounds, called bis(phthalocyanines) are mixed-valence or intervalence compounds, involving a considerable charge transfer, and hence, are of considerable interest as NLO materials. The structure of a metal bis(phthalocyanine) is shown in Figure 11.
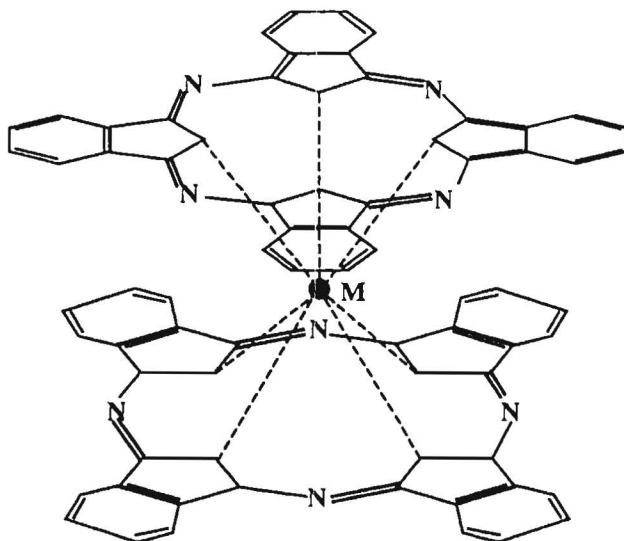
Figure 11 Structure of a Metal Bis(phthalocyanine)[5]

Although the sketch in Figure 11 shows each phthalocyanine ring parallel to each other, x-ray diffraction studies on lutetium bis(phthalocyanine), $LuPc_2$, and neodymium bis(phthalocyanine), $NdPc_2$, have shown that each phthalocyanine ring is rotated 45 degrees with respect to each other and are slightly distorted from planarity[6].

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[5] *Journal of Physical Chemistry*, Vol. 96, No. 14, 1992
[6] DeCian, A., Moussavi, M., Fischer, J., Weiss, R., *Inorganic Chemistry*, V. 24, p. 3162 (1985).

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5.0 OPTICAL CHARACTERIZATION OF ORGANIC OPTICAL LIMITERS

There are two techniques that are commonly used to characterize the nonlinear optical performances of films. The first is a single-beam technique called the Z-Scan, developed by M. Sheik-Bahae, A.A. Said, and E.E. Van Stryland, and is used to measure the nonlinear refractive index and the nonlinear absorption coefficient of materials. In this technique, an expanded, collimated Gaussian laser beam is focused and allowed to diverge through a finite aperture placed directly in front of a detector, as shown in Figure 12.
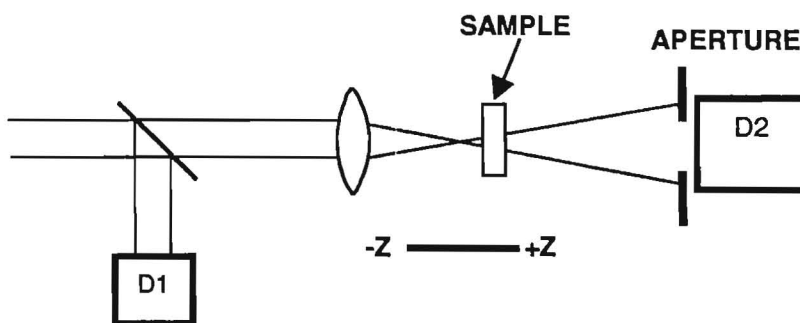
Figure 12 Single-Beam Z-Scan Setup[7]

Another detector measures the incident power transmitted from the laser, using a beam splitter to siphon off a fraction of the beam. A sample film of material, with thickness less than the depth of focus of the beam, is placed well in front of the focus and is moved toward it. From inspection of the following equation, it can be seen that as the sample is moved from the left toward the focal point of the lens, a positive nonlinear effect from the film will result in a negative lensing effect, thereby increasing the transmittance through the aperture.

Equation 24
$$n = n_0 + \frac{n_2}{2} E^2 = n_0 + \Delta n$$

To the right of the position of the focal point, the negative lensing effect of the sample increases the divergence of the beam, resulting in a reduction in the transmittance through the aperture. The opposite is true for a negative nonlinear effect. Scanning the sample and recording the transmitted power at each position produces a plot similar to that shown in Figure 13 for a positive lensing effect and one similar to that in Figure 14 for a negative lensing effect.

The magnitude of the nonlinear refractive index can be calculated by analyzing the thin film medium. The magnitude of a Gaussian beam travelling in the positive z direction may be defined by the factoring equation:

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[7] Sheik-Bahae, M., Said, A.A., Van Stryland, E.W.; **High Sensitivity Single Beam n2 Measurements,** *Optics Letters,* 14, pp. 955-957, 1989 .

Equation 25
$$\left|E(r,z,t)\right| = \left|E_0(t)\right| \frac{w_0}{w(z)} Exp\left[\frac{-r^2}{w^2(z)}\right] \; ,$$

where $w^2 = w_0^2(1 + z^2/z_0^2)$ is the beam radius at position z, $z_0 = kw_0^2/2$ is the diffraction length of the beam, k is the wavevector, and w_0 is the beam waist ($1/e^2$). Neglecting diffraction and nonlinear refractive effects (allowable for a thin film), the change in the amplitude of the beam due to the film is

Equation 26
$$\frac{d\left|E\right|}{dz} = -\frac{\alpha}{2}\left|E\right|$$
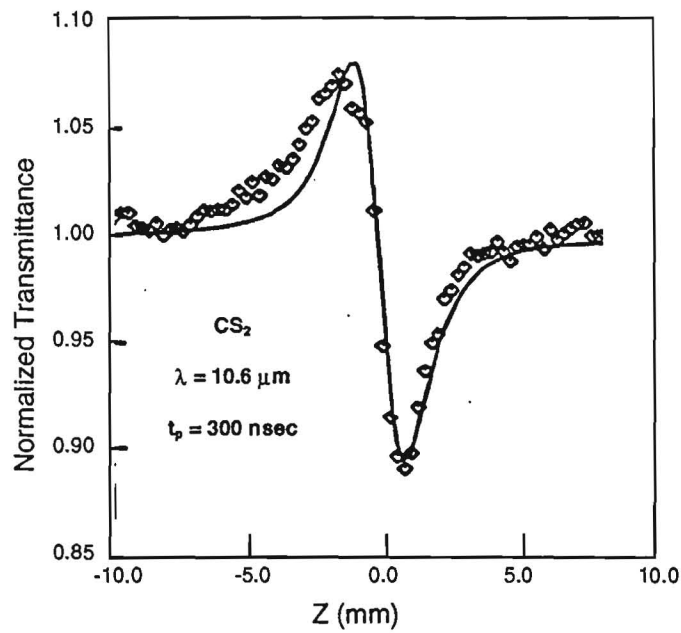
Figure 13 Typical Z-Scan Plot for a Positive-Lensing Material.
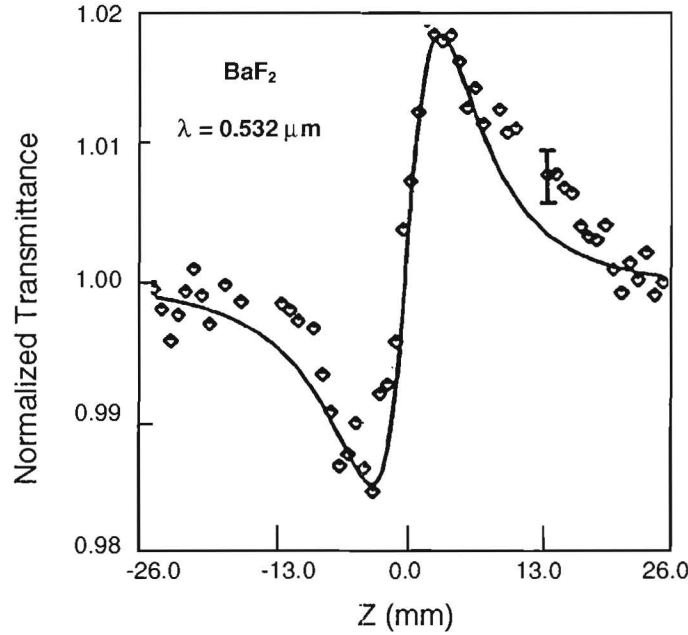
Figure 14 Typical Z-Scan Plot for a Negative-Lensing Material.

The change in phase is

Equation 27
$$\frac{d\Delta\phi}{dz} = \frac{2\pi\Delta}{\lambda}$$

Here, α is the linear absorption coefficient for the material. The phase shift at the exit surface is radial in nature and is given by

Equation 28
$$\Delta\phi(r, z, t) = \frac{\Delta\phi_0}{1 + z^2/z_0^2} \exp\left[\frac{-2r^2}{w^2(z)}\right]$$

Where

Equation 29
$$\Delta\phi_0 = \frac{2\pi\Delta n_0(t)}{\lambda} \frac{1 - e^{-\alpha L}}{\alpha}$$

Here, L is the thickness of the film. When there is no absorption, the term $(1-e^{-\alpha L})/\alpha$ reduces to L. It has been shown that the difference between the normalized maximum and minimum transmittances is approximately equal to $0.405(1-S)^{0.25}\Delta\phi_0$, where S is the relative aperture size and S = 1 implies a large aperture or no aperture. Therefore, from

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the Z-scan plot, one can obtain the value for $\Delta\phi_o$ and calculate Δn_o. From this, then, the higher-order nonlinear refractive index can be obtained.

Figure 15 shows six sets of data points taken during a Z-scan with no aperture. Each set of data corresponds to a different laser energy. When the Z-scan measurements are conducted in this way, the nonlinear absorption coefficient for the material can be obtained, from which the two-photon cross-section can be calculated. Using the transmittance at position $z = 0$, i.e. at the focal point of the beam, for each set of data, the nonlinear absorption coefficient, β, can be found by integrating the expression
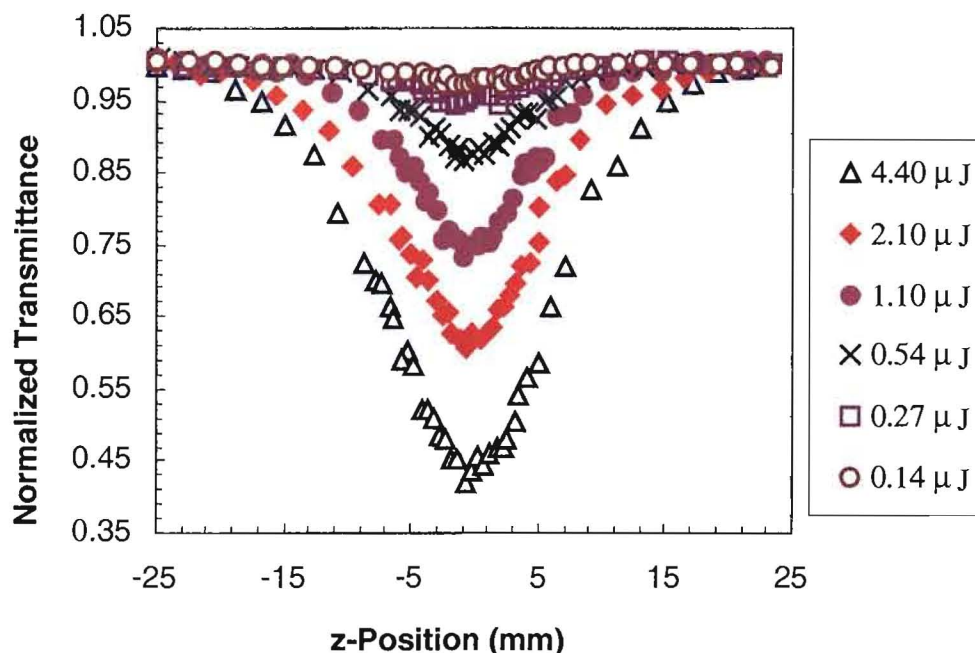
Figure 15 Open Aperture Z-Scan Measurements[8]

Equation 30
$$T = \frac{1}{\beta L_{eff} I_0 \sqrt{\pi}} \cdot \int_{-\infty}^{\infty} \ln\left[1 + \beta L_{eff} I_0 \exp\left(-x^2\right)\right] dx$$

where I_o is the laser irradiance in W/cm^2 and is equal to

Equation 31
$$\frac{2E}{\pi^{3/2} w_0^2 \tau}$$

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[8] Sutherland, R., McLean, D., Lalgudi, N., Brandelick, D., Brant, M., Bunning, T., Fleitz, P., Tondiglia, V., Epling, B.; **SAIC Laser Hardened Concepts III**, Final Report, U.S. Air Force Contract No. F33615-90-C-5911, p. 186, Dec 1995

and τ is the pulse width of the laser. For small nonlinear absorption the following approximation can be used to determine β

Equation 32
$$\Delta T \approx \frac{\beta}{2\sqrt{2}} I_0 L_{eff}$$

where ΔT stands for the difference in the maximum and minimum transmittance. The two-photon scattering cross-section is related to the nonlinear absorption coefficient by $\sigma_2 = \beta \leq \varphi/N$, where N is the molecular number density.

5.1   Degenerate Four-Wave Mixing

Another technique used to characterize the nonlinear properties of materials is degenerate four-wave mixing (DFWM). In this technique, the interaction of two or three (depending upon the geometry) coherent light beams induces a nonlinear polarization in a medium through the third-order term in the susceptibility. The induced polarization then generates a fourth coherent beam. In DFWM the input beams have the same angular frequency, φ, and so the polarization, and the generated beam, also oscillate at φ. DFWM can be thought of as the process where two laser beams form an interference pattern, producing an index of refraction grating within a medium. A third beam, called the probe beam, is diffracted off this index grating and the signal from it measured. In this way, the magnitude of the components of the third-order susceptibility tensor can be found relative to a reference susceptibility (usually CS_2). An example of a DFWM setup is shown in Figure 16.

There are many possible geometrical arrangement for DFWM, but the two most common are the forward mixing and backward mixing geometries. In the forward mixing geometry, shown in Figure 17, the pump and probe beams intersect at small angles inside the nonlinear medium and give rise to a nonlinear polarization that re-radiates a signal field at frequency   in the phase-matched direction $k_4 = 2k_1 - k_3$, where the bold face type represents vector quantities. The magnitude of the nonlinear polarization equals (3 ε_0 $\chi^{(3)}/4$) $|E_1|^2 E_3^* e^{i \Delta kz}$. Δk is a term known as the phase mismatch and arises because the phase of the polarization component is not constant throughout the medium. What happens instead is that phase fronts, with constant phase φ/k, move through the medium. Although the polarization does not actually move in space, these phase fronts give rise to the term "polarization wave".
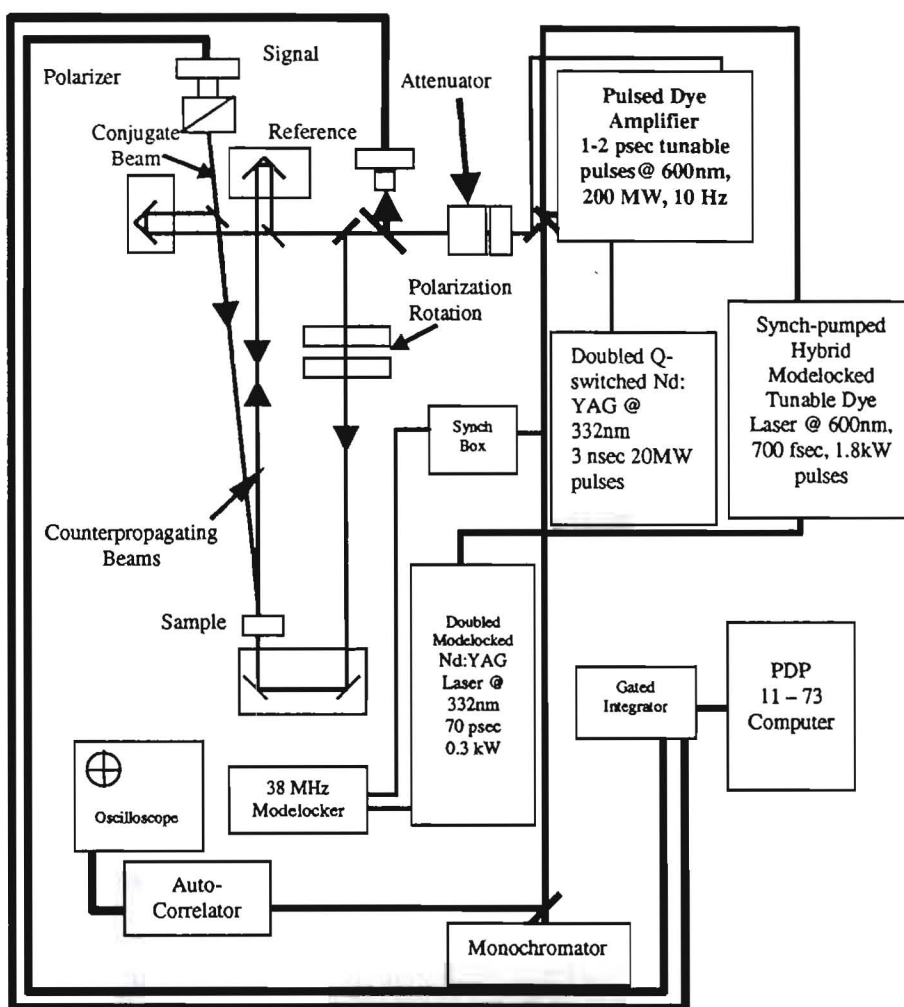
Figure 16 An Example Of A Degenerate Four-Wave Mixing Setup[9]

When the pump beam is more intense than the probe, the evolution of the pump beam can be decoupled from that of the signal and probe. As a result, a solution of the wave equation can be formulated to give the magnitude of the pump beam for every point, z. This solution is given by

Equation 33
$$E_{pump} = E_{pump}(0) \cdot \exp\left[i\gamma I_{pump}(0)z_{eff} - \alpha\frac{z}{2}\right]$$

where I_{pump} is the intensity of the pump beam incident on the medium, $\gamma = (3\,\varphi/2n^2\,\varepsilon_o c^2)\,\chi^{(3)}$, n is the index of refraction, ε_o is the linear absorption coefficient, and the effective magnitude, $z_{eff} = 2(1-e^{-\alpha z/2})/\alpha$. The real part of α represents the intensity-dependent change in the refractive index while its imaginary counterpart represents two-photon

[9] Sounik, J., Norwood, I., McCulloch, K., Song, R., DeMartino, R., Charbonneau, L., Yoon, H., **Development of Organic Optical Materials**, Final Report, AFOSR, Contract No. F49620-89-C-0097, Oct 1992.

absorption. Using this term in the coupled wave equations for the probe and signal beam yields for the probe:

Equation 34
$$I_{probe} = \frac{I_{pump}(0)e^{-\alpha L}}{[1 + Im(\gamma)I_{pump}(0)L_{eff}]^2} + I_{signal}(L)$$

and for the signal beam:

Equation 35
$$I_{signal} = \frac{I_{probe}(0)\gamma^2 I_{pump}^2(0)L_{eff}^2 e^{-\alpha L}}{2[1 + Im(\gamma)I_{pump}(0)L_{eff}]^3}$$

Physically, this can be interpreted as an interference pattern between the pump and probe beams, with the real parts of the equations governing refractive index and the imaginary parts governing amplitude gratings.
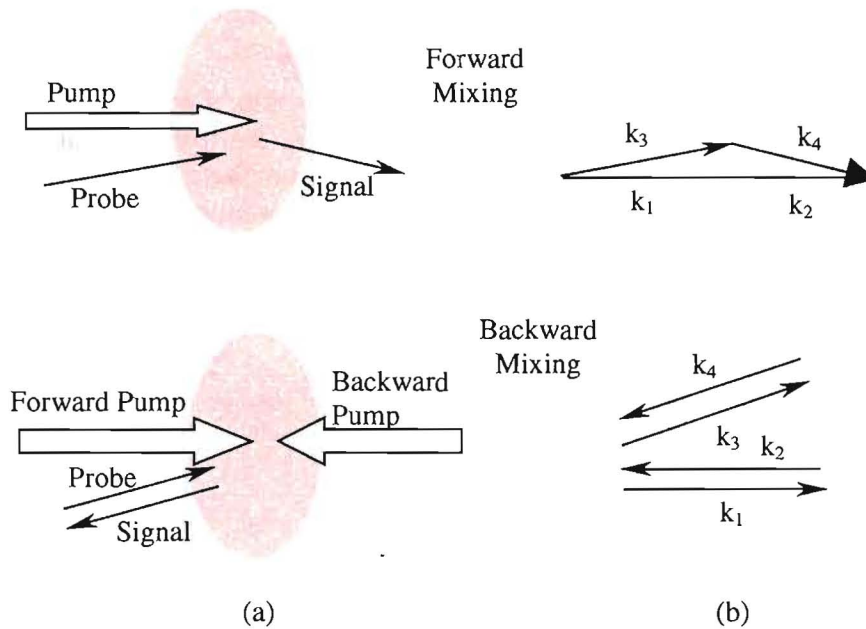
Figure 17 Forward and Backward DFWM Geometries.

In the backward geometry, which is also shown in Figure 17, two collinear and counter-propagating pump beams and a weaker probe beam are directed into the medium. As in the forward case, a nonlinear polarization generates a signal beam, but in this case, the phase matching condition is $\Delta k = 0$. Under this geometry, $\mathbf{k_2} = -\mathbf{k_1}$. Hence, also $\mathbf{k_4} = -\mathbf{k_3}$. The latter relationship implies that the signal beam retraces the exact same path taken by the probe, with the opposite phase. This phenomenon is known as phase conjugation or time reversal.

31

In any DFWM experiment, the quantity that is measured is the intensity of the signal beam. The dependence of the signal beam on the incident pump intensity is measured. What is commonly done is to first perform an identical experiment on a CS_2 reference and then on the experimental material (instead of fitting this dependence to a cubic plus linear expression to yield the nonlinear susceptibility). The third-order susceptibility of CS_2 is well known (6.8×10^{-13} esu at 532 nm) and the susceptibility of the material in question can be calculated using the expression

Equation 36
$$\chi^{(3)}_{sample} = \chi^{(3)}_{ref} \left(\frac{C_{sample}}{C_{ref}} \right)^{\!1/2} \left(\frac{n_{sample}}{n_{ref}} \right)^{\!2} \left(\frac{L_{ref}\,\alpha_{sample}}{1 - e^{-\alpha L}\, e^{-\alpha L/2}} \right)$$

where C_{sample}, C_{ref} are the coefficients of a cubic least-squares fit of the phase conjugate signal versus the pump intensity, L is the sample path length, and α is the linear absorption coefficient.

A method similar to DFWM is referenced in a paper by Maker et. al.[10] and is referred to as the Maker-Fringe experiment. An optical parametric oscillator (OPO) was pumped by a frequency-tripled, Q-switched Nd:YAG laser. The pump laser was pulsed at 10 Hz with a 7 ns pulse duration. The OPO further shortened the pulse width to 4 ns. The maximum pulse energy for this experiment did not exceed 2 mJ.

The sample was mounted on a rotary sample stage within a vacuum cell to avoid contributions from the air. The laser beam is split into two legs, one impinging onto the test sample and the other onto a quartz reference. From here, each third-harmonic generated signal passed through a monochromator to a photomultiplier tube with a boxcar averager. The value of $\chi^{(3)}$ for the test sample was calculated by referencing the signal from the test sample to that of the reference with the following equation:

Equation 37
$$\chi^{(3)} = \frac{2L_{cr}\,P_{ms}^{1/2}}{\pi L_{s}\,P_{mr}^{1/2}} \chi_{r}^{(3)}$$

where

L_{cr} is the coherence length of the quartz reference,

L_{s} is the thickness of the test sample,

P_{ms} is the absorption-corrected THG signal from the sample beam

P_{mr} is time measured intensity from the reference beam.

P_{ms} is related to the measured THG signal by

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[10] Maker, P.D., Terhune, R.W., Nisenoff, M., and Savage, C.M., *Physics Review Letters*, V. 8, p. 21, (1962).

Equation 38
$$P_{ms} = P_m \left(\frac{\alpha L_s / 2}{1 - e^{-\alpha L_s / 2}} \right)^2$$

where $\alpha L_s / 2$ is the sample absorbance.

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## 6.0   IMPLEMENTATION OF SENSOR AND EYE PROTECTIVE OPTICAL LIMITERS

Phthalocyanines and porphyrins are representative of passive nonlinear absorptive limiters which protect human eyes and other focal plane sensors from damage by pulsed laser radiation. In this application, the term 'passive' implies that optical energy is used to cause the material to absorb, refract, deflect or scatter the beam at high input energies or powers. These materials exhibit the properties of reverse saturable absorption (RSA), which occurs when states with an absorption cross section in excess of the ground state cross section are produced. The effectiveness of RSA molecules for optical limiting is determined mainly by the ratio of these cross sections which is a function of wavelength and the population of the states that evolve during the pulse. In the case of optical limiting, it is desirable to have a region of low attenuation for linear input fluences followed by a region of induced attenuation as the radiance increases, and finally a safe region of low transmission. To date, no materials have exhibited sufficiently strong nonlinear response to demonstrate limiting without optical gain (i.e., focusing to concentrate the light in the material).

6.1   Sensor Protection

An example of using one of these materials to protect a detector is provided by situating an aperture behind the nonlinear material, located at or near the focal plane of a lens. The diameter of the aperture is made sufficiently large to capture most of the low-irradiance light, however, as the irradiance increases, nonlinear absorption effects cause reduction in the transmittance. In addition, nonlinear diffraction effects distort the beam profile before it reaches the aperture, thus causing further transmittance reduction at the detector. In an imaging system, the aperture can be placed at an intermediate focal plane.

An example of an f/5 optical limiter is shown in Figure 18[11]. This limiter utilizes both refractive and absorptive nonlinearities. Lens L1 focuses the beam to a near-diffraction limited spot. Light passing through the limiting material is recollimated by L2. The apertures A2 and A3 define the f/5 optics throughout the limiter. A1 acts as a baffle. L3 gives a soft focus onto the detector (Det).

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[11] Shirk, J.S., Pong, R.G.S., Bartoli, F.J., Snow, A.W., **Optical Limiter Using A Lead Phthalocyanine**, *Applied Physics Letters*, 63, 14, pp. 1880-1882, 4October (1993).
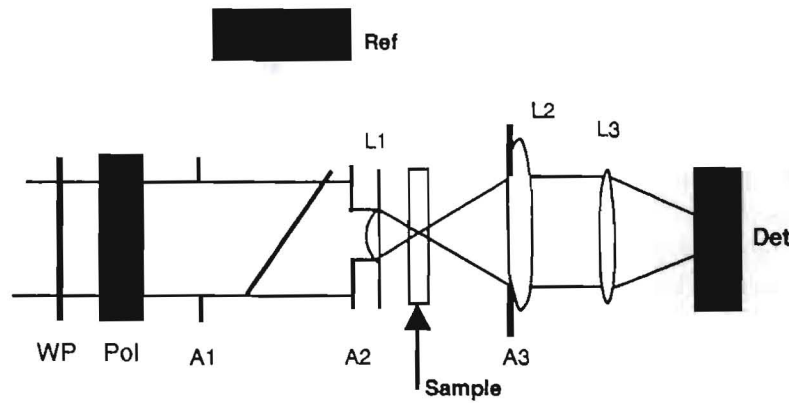
Figure 18 f/5 Optical Limiter[12]

Unfortunately, the nonlinear elements (the optical cell that holds the liquid or the solid host in which the material is dissolved) may also suffer laser induced damage for high inputs. The strongest nonlinear response can be obtained by placing the nonlinear material at the focus. However, from a practical viewpoint, the material is likely to be damaged at this position, resulting in reduction of dynamic range, or DR (i.e., the linear transmittance divided by the lowest transmittance, which occurs at high inputs). This has prompted researchers to devise means of protecting the limiter from damage by placing the nonlinear material in front of the focus, thus achieving a compromise between DR and threshold. Designs to optimize the tradeoff have been studied (e.g. by tandem elements or by graded elements[12,13]). In the case of tandem limiters, the elements are placed upstream in a way that protects the next element down stream (and closer to focus) from damage. Therefore, at the highest input, each element operates below the damage threshold. Here, the front surface of each element operates at threshold, but within any element the fluence drops due to absorption, and is therefore not optimally utilized. When the graded density limiter is used, each differential element along the propagation direction of nonlinear material protects the downstream portion from damage; thus all the nonlinear material operates at the damage threshold. The tandem limiter was originally utilized to keep a low limiting threshold but increase its dynamic range. On the other hand, the graded density limiter, which ignores the threshold and low-input operation, was used in situations that focused at the high energy input, and kept the output for such an input below a fixed value determined by damage to optical components. In the end, the two viewpoints give identical results for tandem limiting. In addition, in the limit where the number of elements in a tandem limiter becomes large, the difference between a tandem limiter and a graded density limiter vanishes.

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[12] Xia, T , Hagan D.J., Dogariu, A. Said, A.A., Van Stryland, E.W., **Optimization Of Optical Limiting Devices Based On Excited State Absorption**, *Appl. Opt.*, Vol 36, No. 18, pp.4110-4122, 20 June (1997).
[13] Miles, P.A., **Bottle Neck Optical Limiters**, *Appl. Opt.*, Vol 33, No. 30, pp. 6965-6979, 20 October (1994).

6.2   Eye Protection

The development of devices to protect the human eye from damage during its illumination with visible laser pulses requires the simultaneous consideration of several physical and operational aspects of the problem[14]. First, there is the size and dynamics (pulse shape) of the specific laser threat to be faced. This threat must be judged with regard to the susceptibility of the retina to damage and its dependence on pulse length, wavelength and irradiated area. Second, the design of the optical system in which protection is to be provided must be examined to make sure that its normal (nonlaser) function is not appreciably degraded. Finally, the protective device itself is likely to be susceptible to laser damage unless the device is properly designed to withstand the full extent of the threat or threat pulses.

Reference 14 cites that the dependence of the retinal damage threshold on the irradiated area shows that the damage process itself is not simply a function of the fluence at any one point. Rather the damage threshold fluence decreases as an inverse of the spot diameter, while the threshold fluence increases only linearly with spot diameter. The latter result was interpreted therein, as a reason to employ purely absorptive mechanisms for eye protection, and avoid protective devices that spread the input beam without significant attenuation. Excited state absorption in phthalocyanines and porphyrins provide this type of fluence- dependant nonlinearity. Beam spreading is a weak protection. It can also be completely eliminated by inadvertent refocusing of the eye itself. While limiting has been achieved in high f/# optics, the performance of current state-of the-art devices is inadequate for eye protection at anticipated threat levels, whereas attempts to use low f/# optics have resulted in damage to the limiter itself. Thus, schemes employing tandem and graded limiting materials (bottleneck limiters) find application in eye protection as well as sensor protection.

6.3   Solid State Limiters

Liquid state limiters utilize a solvent as the matrix for the nonlinear dopant material. While liquid state limiters may have the advantage of self healing if damaged by the laser beam, the incorporation of these materials into a solid state host has many advantages such as the fabrication of monolithic lens/limiter optical components, thin film coatings and improvement in damage threshold through introduction of concentration gradients. The realization of such solid state applications requires addressing issues of morphology, film processing and limiter activity and stability.

6.3.1   Thin Films from Organic Materials
NLO susceptibilities have been reported through research on solutions of porphyrins and phthalocyanines or from Langmuir-Blodgett films. However, in order for the NLO organic materials to be useful for optical limiting applications, they must be incorporated into solid-state materials that have a high damage threshold and that are optically transparent at whatever desired band(s) are necessary under low power conditions. Two of the more common materials that have been investigated for use as a solid matrix for these materials are polymers such as polymethylmethacrylate (PMMA) and composite glasses produced by the

sol-gel process. Materials such as PMMA are easily obtainable, thus making the production of optical film with PMMA an easy matter. The NLO material in a solvent is mixed with the polymer and spin coated onto a substrate. Then the NLO is baked on a hot stage. However, because of its low damage threshold, the use of PMMA is limited.

Sol-gel films are made by doping silica gel with the organic compound in a solvent. The gel is allowed to cure and is heated to achieve a fully dense glass. To make the glasses into optical windows, they are cast into molds having optically flat ends.

The higher damage thresholds of sol-gel materials were thought to make them a more robust matrix, but it has been recently reported that the ability of materials to withstand laser damage is proportional to the mechanical damage thresholds of those materials. That is, a material that has a high mechanical damage threshold has been shown to also have a high laser damage threshold. Therefore, the emphasis is shifting towards the development of more elastic matrices. For instance, the phthalocyanine compounds produced by Boyle and Snow may be heated into viscous liquids and mechanically pressed between flat surfaces into supported or free-standing films for optical applications[5].

6.3.2   Research on Solid-State Matrices
One approach to achieving a film with a glassy morphology (obtained by chemically functionalizing the ring periphery of metal free and lead phthalocyanines with an amine-epoxy substitution) has been explored[14]. Uniform films were reported, obtained by a shearing technique. Comparative optical measurements were made on the amine-epoxy lead phthalocyanine compound as a concentrated solution and as the glassy thin film. Both the solution and the film exhibited reverse saturable absorption at wavelength of 590 nm. While the concentrated solution was found to be a very effective optical limiter, the thin film was susceptible to damage (cavitation caused by the incident beam) and performed comparably only at low energies.

The performance of a solid state limiter based on a Pb/Pc/urethane copolymer was studied using degenerate 4-wave mixing and nonlinear transmission experiments in the visible and near-IR (1064 nm) and by transient absorption spectroscopy[15]. Results showed that polymers of this type are processable into a solid matrix and can achieve efficient optical limiting. Furthermore, their molecular structure can be modified to control the physical and optical properties of the material.

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[14] George, R.D., Snow, A. W., Shirk, J.S., Flom, S.R., Pong, R.P.S., **Preparation Of Thin Film Phthalocyanine Glasses For Optical Limiting**, *Materials For Optical Limiting Research Society Symposium*, Proceedings Vol. 374, pp. 275-280 (1995), Materials Research Society, Pittsburgh, Pa.
[15] Shirk, J.S., Boyle, M.E., Adkins, J.D., Pong, R.D.S., Richard, G.S., Flom, S.R., Steven, R. Lindle, J.R., **Polymeric Thin Film Optical Limiters**, *Proceedings Of The Conference On Lasers And Electro-Optics*, pp. 418-419, Anaheim, Ca. (1994).

Solid host materials such as poly-methylmethacrylate (PMMA) and organically modified sol-gels have been doped with phthalocyanines[16]. Soluble silicon phthalocyanine (SiPc (OC//7H//1//5)) was introduced into PMMA. A comparison between the nonlinear absorption of the compound in solution and the doped solid matrix demonstrated that broadband solid state limiters can be achieved for visible nanosecond-pulse excitation.

Nanosecond nonlinear absorptive properties and excited-state properties such as the triplet-triplet absorption spectrum and triplet quantum yields of metallophthalocyanines introduced into organically modified sol-gels have been shown to be similar to those in solution[17]. Sol-gel processing is a solution based technique for preparing porous metal oxide monoliths at low temperatures. By adding phthalocyanine to the precursor solution, one can trap these organic molecules in the pores of a silica host. It has been shown that such phthalocyanine doped glassy materials are stable and exhibit optical nonlinearities comparable to those of the corresponding solutions[18]. As an example, the retention of aluminophthalocyanine molecules trapped in solid xerogel matrices was demonstrated by duplication of properties in solution, i.e., reverse saturable absorption at a wavelength of 532 nm in nanosecond and picosecond regimes[19].

An approach to increasing the bulk laser damage thresholds of solid state hosts is to tailor their viscoelastic properties, for instance their shear modulus and glass transition temperature, to better dissipate absorbed energy. Approaches to achieving this goal have been implemented using softened epoxy as the host[20] and gelatin with a water soluble copper (II) phthalocyanine- tetrasulfonic acid, tetrasodium salt (CuPcTs)[21]. The viscoelastic gelatin has mechanical properties which are different from those of a liquid or a solid. Laser measurements demonstrated that the single shot damage threshold of the undoped gelatin host increases with decreasing gelatin concentration. The gelatin has a much higher damage threshold than a stiff acrylic. Unlike brittle solids, the soft gelatin self - heals from laser induced damage. Optical limiting tests also exhibited the

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[16] Barny, P., Dentan, V., Robin, P., Soyer, F., Vergnolle, M., **Broadband Visible Reverse Saturable Absorption In Silicon Phthalocyanine Solution and Polymer**, *Proceedings Of The SPIE*, Vol . 2852, pp. 201-210 (1996).

[17] Mansour, K., Fuqua, P.D., Marder, S.R., Dunn, B.S., Perry, J.W., **Solid State Optical Limiting Materials Based On Phthalocyanine-Containing Polymers And Organically Modified Sol-Gels**, *Proceedings Of The SPIE* , Vol. 2143, pp. 239-250 (1994).

[18] Fuqua, P.D., Mansour, K., Alverez, D., Marder, S.R., Perry, J.W., Dunn, B.S., **Synthesis Of Nonlinear Optical Properties Of Sol-Gel Materials Containing Phthalocyanines**, *Proceedings Of The SPIE*, Vol. 1758, Pp. 499-506, (1992).

[19] Brunel, M., Canva, M., Brun, A., Chaput, F., Boilot, J., **Reverse Saturable Absorption Behavior Of Aluminophthalocyanine-Doped Xerogels**, *Proceedings Of The Conference On Lasers And Electro-Optics*, Vol. 8 (1994).

[20] Brant, M.C., DeRosa, M.E., Hao, J., McLean, D.G., Sutherland, R.L., Campbell, A.L., **Guest Host Optical Limiters With High Laser Damage Threshold**, *Proceedings Of The SPIE*, Vol. 2996, pp. 88-95 (1997).

[21] Brant, M.C., McLean, D.G., Sutherland, R.L., DeRosa, M.E., Campbell, A.L., Martinez, S., **Laser Damage Threshold Of Gelatin and a Copper Phthalocyanine Doped Gelatin Optical Limiter**, *Proceedings Of The SPIE*, Vol. 2714, pp. 33-40,(1996).

advantages of a gelatin host doped with CuPsTs. The CuPtTs/gelatin matrix is not damaged at incident laser energies five times the single shot damage threshold of the gelatin host. However at this high laser energy, the CuPsTs is photobleached at the beam waist. The photo bleached sites were shown to be repairable by annealing.

6.4 Molecularly Engineered Optical Properties

For optical limiters to play a useful role in addition to limiting throughput and surviving high laser intensities, they must have low-intensity spectral transmittance characteristics consistent with the optical system in which they are introduced to protect. Rational design of optical limiter chromophores requires knowledge of the relation between structure and limiting behavior. The accurate prediction of such requires first principle methods and computational hardware and software capabilities which have recently advanced to the stage at which such calculations are feasible[22]. Work to develop a structure/optical property data base is currently in progress. Such a database could be applied to calibrating and validating molecular models and learning what factors influence limiting behavior[23].

For instance, in a daylight direct view, optical systems should have a broadband transmittance similar to a photopic eye response (i.e. color neutrality). *Unfortunately, most measurements of optical limiting are carried out at a single wavelength (commonly 532 nm).* However, work has been pursued to engineer molecules for the enhancement and spectral tuning of the optical limiting response of phthalocyanine and porphyrin complexes[23,24,25]. Explored structural variations include insertion of metal ions, extension of conjugation halogenation and formation of multimers. It has been demonstrated that the spectral band over which the material exhibits reverse-saturable absorption and limiting can be systematically altered by chemical substitution[24]. The spectral window over which the limiter operates can be engineered by altering both the main ring in the molecular structure and by peripheral substitution of the molecules[25]. As an example, donor substitution of napthalocyanines has been shown to shift the optical limiting response into the red range. This is demonstrated in the case of indium and tin octabutoxynapthalocyanines[26].

[22] Day, P.N., Wang, Z., Pachter, R., **Modeling The Effects Of Solvation On The Structures And Properties Of Optical Limiting Materials Using Ab Initio Quantum Chemistry**, *Mat. Res. Soc. Symp. Proc.*, Vol. 479, pp. 307-312 (1997).

[23] Su, W., Cooper, T.M., Tang, N., Krein, D., Hao, J., Brandelik, D.M., Si, J., Pachter, R., **Structure Optical Property Relationships Of Porphyrins**, *Mat. Res. Soc. Symp. Proc.*, Vol. 479, pp. 313-318 (1997).

[24] Shirk, J.S., Pong, R.G.S., Flom, S.R., Boyle, M.E., Snow, A.W., **Wavelength Dependence Of Reverse-Saturable-Absorption Optical Limiters**, *Conference On Lasers And Electro-Optics*, pp. 334-335 (1995).

[25] Shirk, J.S., Pong, R.G.S., Richard, G.S., Flom, S.R., Bartoli, F.J., Boyle, M.E., Snow, A.W., **Lead Phthalocyanine Reverse Saturable Absorption Optical Limiters**, *Pure And Applied Optics: Journal Of The European Optical Society*, Patr A, Vol. 5, No. 5, pp. 701-707, 5 Sept. (1996).

[26] Perry, J.W., Mansour, K., Marder, S.R., Chen, C.T., Miles, P., Kenney, M.E., Kwang, K., **Approaches For Optimizing And Tuning The Optical Limiting Process Of Phthalocyanine Complexes**, *Materials For Optical Limiting Materials Research Society Symposium Proceedings*, Vol. 374, pp. 257-265 (1995).

Elsewhere it has been demonstrated that optical limiting in the visible over at least a 220 nm band is achievable in four metal-substituted phthalocyanines (MPCs)[27]. In this work, the desire for broadband linear transmittance at low intensities imposed a fixed integrated photopic transmittance of 70%, which determined solution concentration. The results suggest that MPC's with linear transmittance best adapted to the day vision response and good RSA properties (heavy metal substitution), as $GaPc_2$, will allow more efficient broadband optical limiting.

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[27] Dentan, V., Robin, P., Soyer, F., LeBarney, P., Huignard, J., **Broadband Visible Reverse Saturable Absorber in Metallo-Phthalocyanines**, *Proceedings of the 1996 Conference On Lasers And Electro-Optics*, CLEO 96, pp. 178-179, (1996).

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